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Facile Photochemical Synthesis of Unprotected Aqueous Gold Nanoparticles

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In recent years, colloidal gold nanoparticles (AuNPs) have been the subject of strong interest in areas of materials science, biotechnology, and organic chemistry for their function as molecular markers, diagnostic imaging, and catalysis.[1] Their synthesis has been performed under a variety of conditions, including traditional citrate reduction,[2] the widely employed Brust−Schiffrin method of two-phase synthesis with thiol stabilization,[3] seeding growth using ascorbic acid,[4] and several thermal and photochemical techniques using thiols,[5] amines,[6] micelles,[7] dendrimers,[8] polymers,[9] and biomolecules[10] as protective agents to aid in their stabilization in aqueous, organic, and thin film media.[11]

In a recent publication, Mirkhalaf et al.[12] emphasize the need for general synthetic approaches that are less reliant on the chemisorption of stabilizing ligands containing soft atoms (S, N, or P) and comment that alternative methods for the preparation of metal and alloy nanoparticle solutions would be advantageous. They report an ingenious method based on the decomposition of aryl diazonium salts that leads to carbon-protected gold and platinum nanoparticles that are stable for weeks.

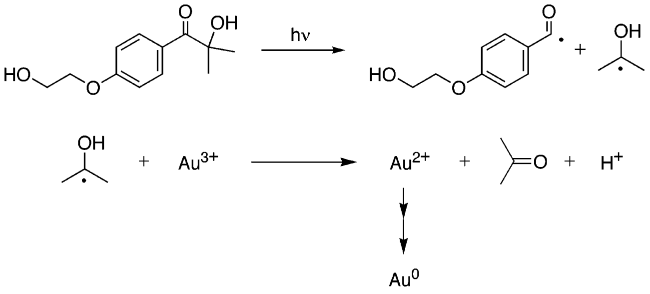
In this communication, we report a photochemical synthesis of stable, unprotected AuNPs that does not require any of the conventional (S, N, or P) stabilizing ligands. One-pot synthesis can be performed in seconds to minutes, rather than hours,[13] under mild conditions using readily available precursors. Further, particle size control can be readily achieved by altering the illumination intensity (vide infra).

Synthesis of aqueous gold nanoparticles was performed using Irgacure-2959 (1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propane-1-one) (I-2959). Upon 350 nm excitation, I-2959 yields ketyl radicals via Norrish-type-I α-cleavage; these ketyl radicals function as reducing agents that are capable of reducing Au^{3+} to Au^{0} and form AuNPs with high spatial and temporal resolution as a result of the photochemical control, as illustrated in Scheme 1.

A slight excess of I-2959 is required to generate enough acetone ketyl radicals, which reduce tetrachloroaurate to form Au^{2+}. This disproportionates to Au^{3+} and Au^{1+}, whereby Au^{1+} is then reduced to Au^{0}, leading to nanoparticle formation.[14] These essentially unprotected NPs are synthesized in minutes in aqueous solution under air and remain stable for months. AuNPs have previously been synthesized photochemically using other ketyl radicals as reducing agents, such as benzophenone[15] or benzoin,[16] but these have been performed in polymers, dendrimers, or micelles and frequently required working under an inert atmosphere. Our method is based in simple aqueous photochemistry, is very rapid, requires no protective groups, and is performed under mild conditions under air.

Gold nanoparticles were synthesized by preparing a solution containing 0.33 mM $HAuCl_4$ and 1.0 mM I-2959 in water.[17] The $HAuCl_4$/I-2959 samples were typically irradiated in a photoreactor with 40 W/m^2 UVA light. Samples were irradiated for a few minutes. The final pH of the ruby-red solution of gold nanoparticles was ~2.5, reflecting the production of acid, as shown in Scheme 1. When the pH is increased to 5.3 and 7.4 by addition of NaOH to afford NPs of approximately the same size, a bathochromic shift in absorbance is observed, consistent with a decreased interparticle distance as revealed by TEM.

Scheme 1. Formation of Gold Nanoparticles



Absorbance spectroscopy of the AuNPs shows a translational surface plasmon band at 530 ± 2 nm, characteristic of spherical AuNPs with high reproducibility. The broader, small peak at 1000 nm may reflect the formation of nanorods. Figure 1 indicates that irradiation for 3 min is sufficient for a significant yield of nanoparticles, when left to ripen for a few hours. Nanoparticles were further characterized by TEM. As shown in Figure 2c, the AuNP's size was 12 ± 3 nm for 40 W/m^2 with good monodispersity. Closer inspection reveals monocrystalline lattices. Unprotected NPs prepared as reported here show remarkable stability in solution for months under ambient conditions, including daily exposure to room lights (inset in Figure 1). Samples were irradiated in either polystyrene BD Falcon 24-well plates or quartz cuvettes and stored in either well plates or capped polycarbonate centrifuge tubes. Use of soda or borosilicate glass appears to reduce the long-term stability of these nanomaterials.

The effect of irradiance on nanoparticle growth was studied; the higher the UVA irradiance and the more uniform the light source, the smaller and more monodisperse the particle size. Exposure to room lights for 3 days resulted in particles of 150−300 nm in diameter. Irradiation of 7, 40, and 100 W/m^2 produced NPs of 40 ± 10, 12 ± 3, and 8 ± 2 nm, respectively, as shown in Figure 2. Preliminary results with inhomogeneous exposure from xenon lamps or pulsed lasers (308 nm) led to increased polydispersity. Notably, nanoparticle formation did not occur in samples stored in the dark.

With no additional capping agent added to stabilize the nanoparticles, their surfaces are relatively unprotected. They are bound electrostatically to the low concentration of anions available in solution, such as chloride and traces of carboxylic acids that may result from oxidative processes of acyl radicals formed in the Norrish-type I cleavage of I-2959. While the fate of substituted benzoyl radicals is not evident from our results, literature reports suggest that, while benzyl radicals can interact with the gold surface,[18] benzoyl radicals are more prone to undergo displacement

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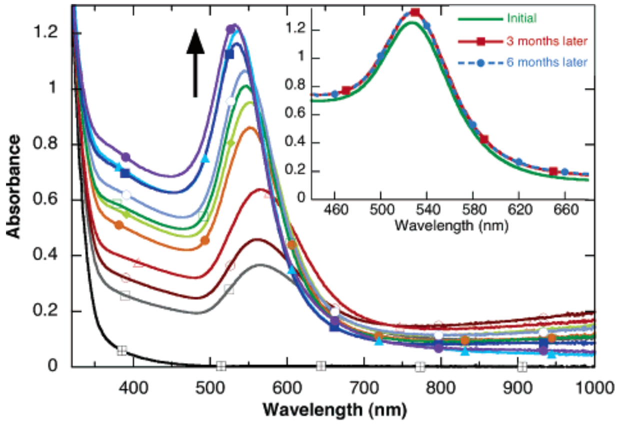

Figure 1. Absorbance of various gold nanoparticle samples prepared with 0.33 mM $HAuCl_4$ and 1.0 mM I-2959 in 24-well plates 40 W/m^2 UVA at 1 min intervals recorded 24 h after exposure. Inset: Stability of a AuNP sample prepared in a polystyrene 24-well plate. Initial absorbance and after 3 and 6 months (overlapping).

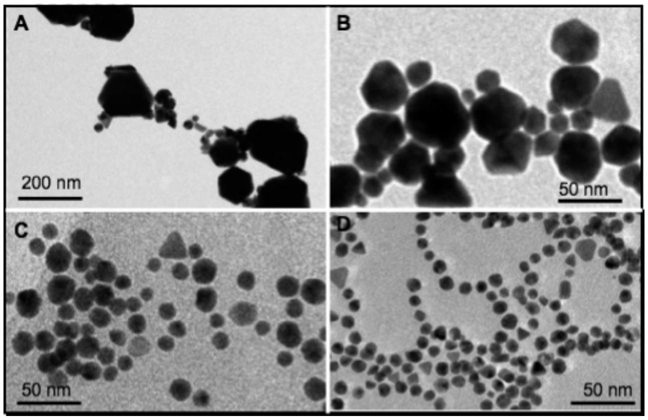

Figure 2. TEM image of AuNPs prepared in a 24-well plate via (a) 3 days room fluorescent light (3% UVA), (b) 7 W/m^2 UVA, (c) 40 W/m^2 UVA, and (d) 100 W/m^2 UVA.

reactions (for example, by binding to and removing thiolate) than to actually attach to the nanocrystal surface.[19] An indication that ion stabilization plays a role was evident from the ease with which the ruby-red solution instantly turned blue upon addition of 3.0 M NaCl; this suggests a decrease in interparticle distance due to the displacement of larger ions (presumably organic) by chloride. This behavior is also reported to occur for citrate-stabilized AuNPs.[20] Further, centrifugation of an untreated red sample at 20 000 rpm resulted in a violet−blue solution upon resuspension and sonication, as a result of NPs in the absence of stabilizing ions. This was confirmed by a negative $AgNO_3$ test for chloride. The resuspended solution is stable for weeks to months.

A key to the rapid and easy synthesis can be attributed to our choice of a benzoin-derived source for the radicals. Benzoin triplet states are known to have subnanosecond lifetimes and as a result are not prone to quenching by transition metal ions.[21] A similar strategy (i.e., short triplet lifetimes) proved valuable in a recent report on the synthesis of silver nanoparticles.[22]

These easily prepared stable AuNPs may prove useful as catalysts, as tools for the study of early processes in NP formation (30 s exposure is sufficient to generate a strong plasmon band), or for custom derivatization as needed when required. These AuNPs can be easily functionalized with water-soluble thiols such as 3-mercapto-1-propane sulfonic acid, sodium salt (MPSA). This is illustrated in Figure 3, showing the change in absorbance as the thiol concentration increases. A longitudinal plasmon forms at higher concentrations, characteristic of nanorod formation identified by TEM.

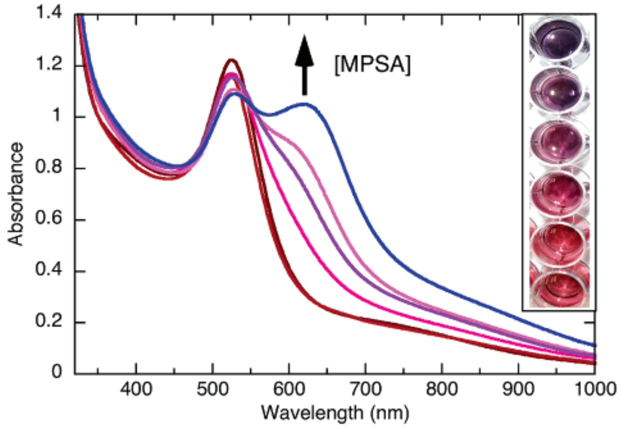

Figure 3. Absorbance of AuNPs after addition of MPSA. AuNPs made from 0.33 mM $HAuCl_4$, 1.0 mM I-2959, and 0−0.33 mM MPSA.

Use of Irgacure-2959 as a photoreducing agent could lead to further applications in lithography with gold, silver, and other coin metals, whereby they could be imaged separately or together as core−shell or alloy nanoparticles.

In summary, stable, unprotected aqueous nanoparticles can be cleanly prepared in minutes by reduction of $HAuCl_4$ by photochemical decomposition of I-2959, a water-soluble benzoin. A wide range of particle sizes can be prepared by controlling the illumination intensity. If required, the particles can be readily derivatized as needed.

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(17) AuNP solutions were prepared with $HAuCl_4 \cdot 3H_2O$ (Sigma) and Irgacure-2959 (CIBA) in distilled, deionized MilliQ water. I-2959 was initially recrystallized using ethyl acetate and stored in an amber bottle. Large batches of solutions were prepared and divided into well plates or quartz cuvettes for consistency. Irradiation took place using a Luzchem LZC-4V or LZC-ORG photoreactor with 1, 6, or 14 UVA lamps.
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